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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Michael Berman/NL AFOSR 875 N. Randolph Street Suite 325, RM 3112 Arlington, VA 22203				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
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# FINAL REPORT PHASE - II STTR

*Air Force Office of Scientific Research (AFOSR)*  
*Contract: FA9550-04-C-0007*

## Microscale Electrospinning of Polymer Nanowires for Sensing Applications

Prepared by:  
Dr. Royal F. Kessick  
Sentor Technologies, Inc.  
11551 Nuckols Rd., Suite Q  
Glen Allen, VA 23060

and

Dr. John Fenn  
Virginia Commonwealth University  
Department of Chemistry  
Richmond, VA 23284

Submitted to:  
Dr. Michael Berman  
Program Manager  
Air Force Office of Scientific Research  
4015 Wilson Blvd.  
Arlington, VA

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## **Program Objectives:**

There is an urgent need for new sensing technologies for battlespace awareness. In particular, new chemical and infrared sensors are required that can provide higher sensitivity and faster response in the field than the existing baseline technologies. The primary objective of this research program is to develop a new solid-state sensor technology with performance parameters (e.g. sensitivity, response time) far surpassing existing systems. The sensing mechanism is conductivity changes in polymeric nanowire arrays produced by exposure to chemical agents or infrared energy. Nanowires represent very promising sensor components due to their very high surface to volume ratio and low thermal mass. The nanowires are produced using a new microscale electrospinning technology developed and demonstrated in the Phase I portion of this research project. In addition to the primary objective of developing a new microsensor technology, part of this research effort will be the investigation and development of a generalized microscale electrospinning technology that can potentially be applied to a wide range of technological problems ranging from advanced sensors to optical computers to new biochips.

## **Status of Effort:**

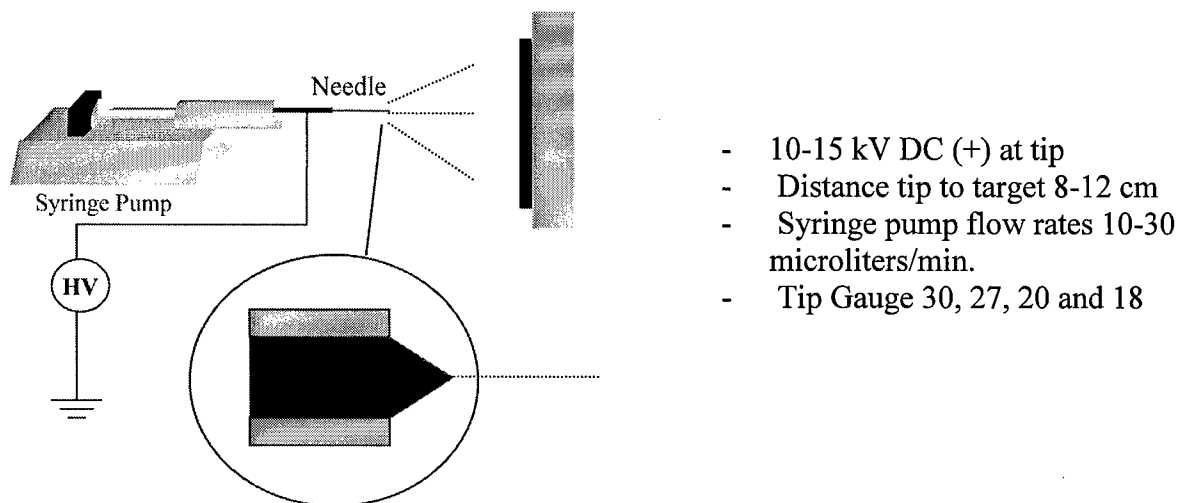
All project tasks have been completed. Prototype chemical and infrared sensors have been fabricated and tested and the performance parameters (presented below) are extremely promising. In addition a new fiber processing technology based on supercritical fluids has been developed and demonstrated. Finally, new polymeric helical structures have been developed and tested and represent a new technology for microscale sensing and actuation. At this time three journal articles (two in *Applied Physics Letters* and one in the *Journal of Supercritical Fluids*) have been published based on this research program and a fourth paper has been submitted to *Sensors and Actuators*. The research results have been presented at four international conferences including the AFOSR Molecular Dynamics and Theoretical Chemistry Conference and the SPIE Defense and Security Symposium. The following sections provide a detailed summary of the program accomplishments and new findings.

## **Accomplishments/New Findings:**

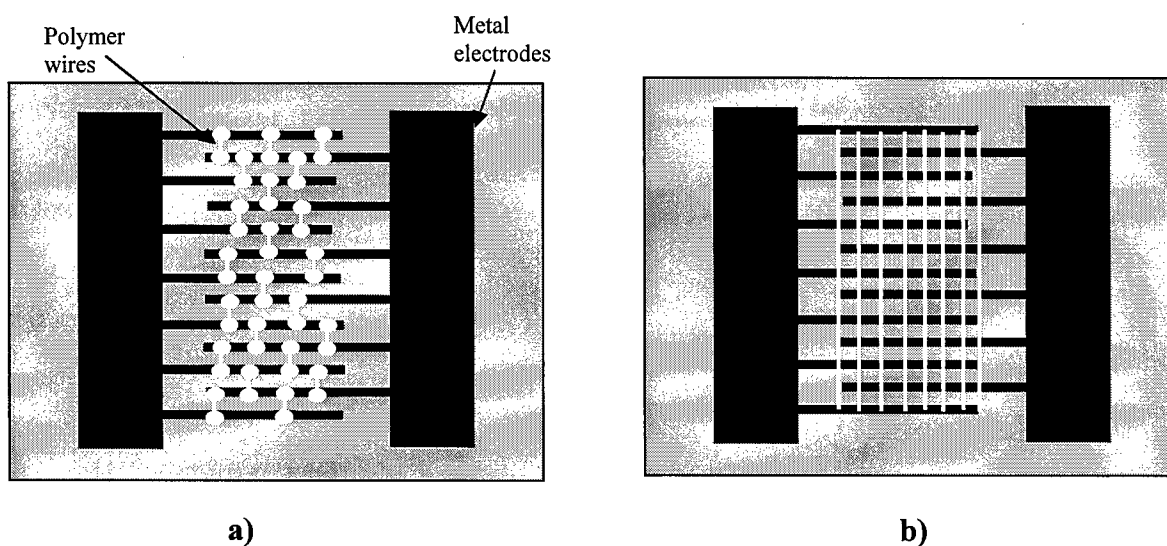
### **Polymeric Nanowire Arrays:**

In electrospinning, an intense electric field is used to draw polymer fibers out of solution. Figure 1 is a schematic diagram of a typical electrospinning apparatus along with the general processing conditions. In the phase I research program we demonstrated that the electrospinning process illustrated in figure 1 can be scaled in order to produce polymer fibers on the surface of a microchip. This work was published and is described in detail in *Applied Physics Letters* (Publication #3 below). Figure 2a is a schematic diagram illustrating the originally proposed device structure consisting of an array of polymeric nanowires interfaced with an interdigitated electrode. In this case, each fiber interconnection is produced individually on the surface of the microelectrode through the application of an electric field. Figure 2b is a schematic illustrating a new device structure that we have successfully developed by carefully controlling the stability of the electrospinning process. We have found that the device structure illustrated in figure 2b can be produced with much higher efficiency, lower cost and with a high degree of

reproducibility. The Phase II effort has focused on the development and testing of advanced chemical and infrared sensors based on the device structure of figure 2b.



**Figure 1: Schematic diagram of electrospinning apparatus and general processing conditions.**



**Figure 2:** Schematic diagram of two sensor device structures consisting of polymeric nanowires on an interdigitated electrode.

The following table lists the specific polymers and solvents that have been investigated to date in this research program as well as an indication of the resulting structure device.

**Table 1: Electrospun Polymers and Solvent Systems**

Polymers	Solvent System	ESP Fibers	Aligned
PVA	Water	Yes	
PEO	Water	Yes	
PEO	Water/Methanol	Yes	Yes
PECH	Chloroform	Yes	Yes
PIB	Chloroform	Yes	Yes
PNVP	Water	Yes	

PVA – Poly(vinyl alcohol)

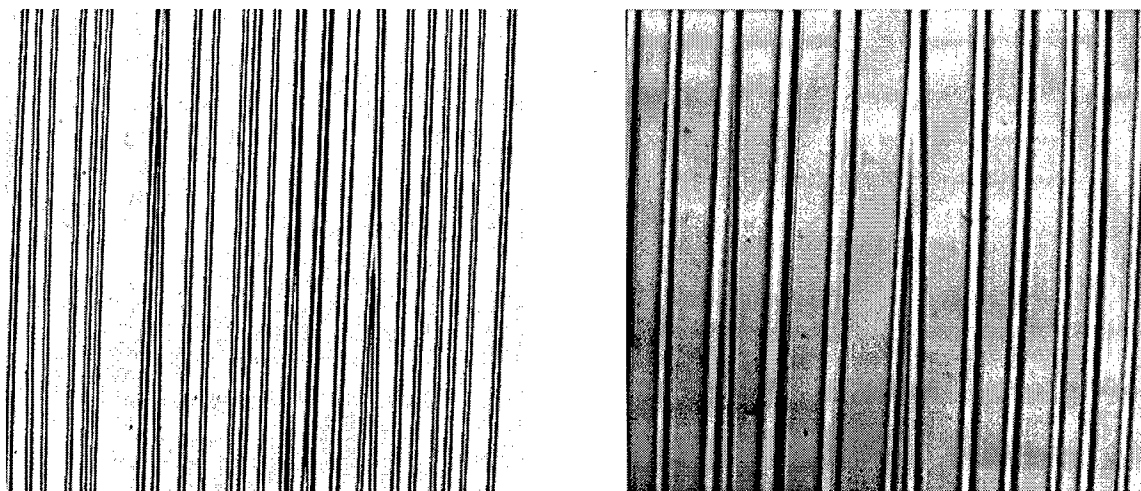
PEO - Poly(ethylene oxide)

PECH - Poly(epichlorohydrin)

PIB - Poly(isobutylene)

PNVP - Poly(n-vinyl pyrrolidone)

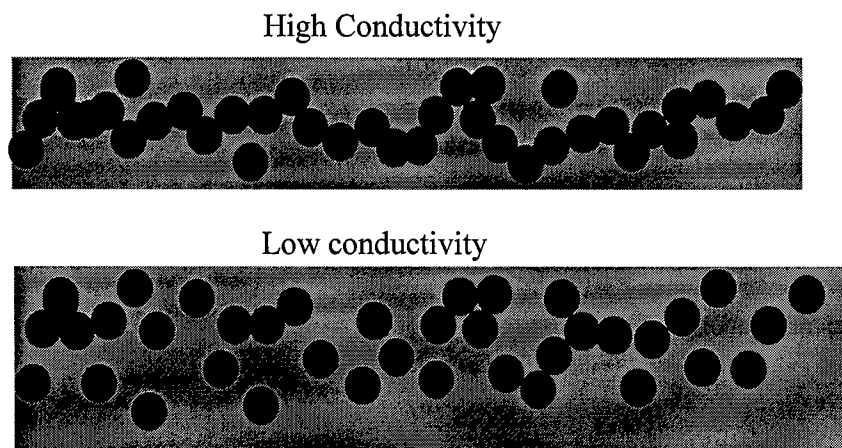
Figure 3 is an optical microscope image of an array of PIB fibers deposited onto the surface of a microscope slide. The electrospun fibers are highly aligned and range from 2-4 microns in diameter.



**Figure 3: Optical microscope image of an aligned array of PIB fibers.**

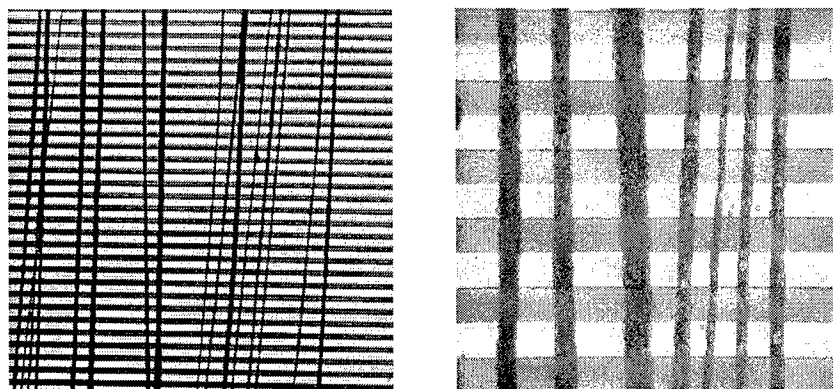
#### **Polymer Composites:**

Fiber arrays consisting of polymers doped with carbon black were developed and tested. The addition of carbon black increases the conductivity of the polymer fibers due to electron transport between the conducting particles. This effect is known as percolation and the electrical resistance of the resulting composite fibers exhibits a very high sensitivity to volumetric changes in the fiber. The sensing mechanism is illustrated in figure 4. The volumetric changes in the fiber are produced by the absorption of chemical vapors or infrared energy as demonstrated in the following section of this report.

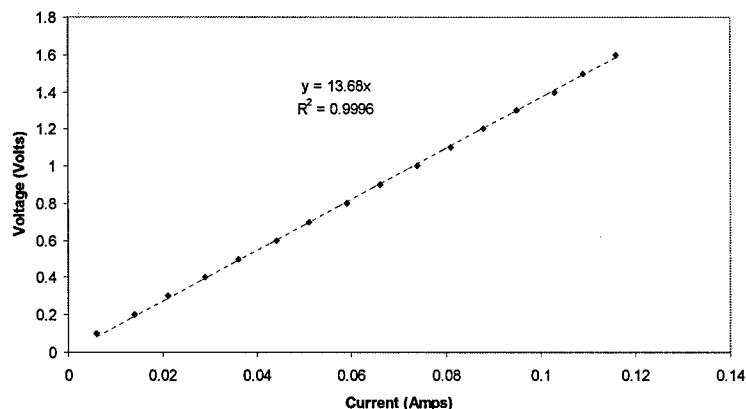


**Figure 4: Schematic diagram illustrating the sensing mechanism of the polymer fiber doped with conducting particles.**

Figure 5 is an optical microscope image of an array of aligned PEO fibers doped with carbon black on the surface of an interdigitated microelectrode. The resistance of the fiber array is approximately 40 ohms and the fiber diameters range from 3-15 microns with coverage of roughly 10 %. Figure 6 is a plot of voltage versus current for the array of figure 4 illustrating the high degree of linearity.

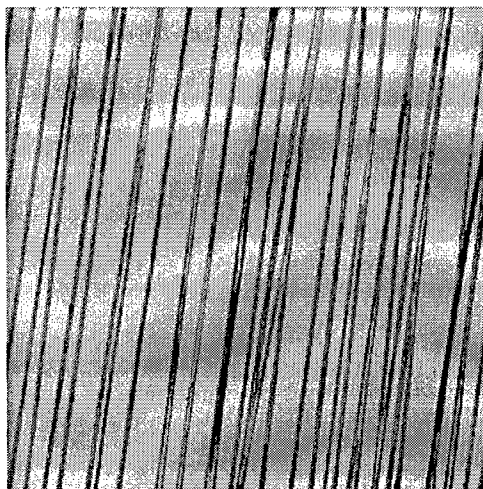


**Figure 5: Optical microscope image of PEO fibers doped with carbon black on an interdigitated microelectrode.**



**Figure 6: I-V curve for the device of figure 5**

Poly(epichlorohydrin) – PECH is an attractive polymer for chemical sensing due to its high affinity to particular volatile organic compounds. Fiber arrays based on PECH doped with carbon black were developed and tested. The final dry weight of the carbon black to PECH is 10/90. Using the general electrospinning conditions the PECH/CB solution formed aligned fibers on both a gold substrate and an interdigitated microelectrode. The resistance of the microchip was measured to be ~ 20 Ohms. Figure 7 is an optical microscope image of the PECH fibers on the gold substrate and microelectrode.



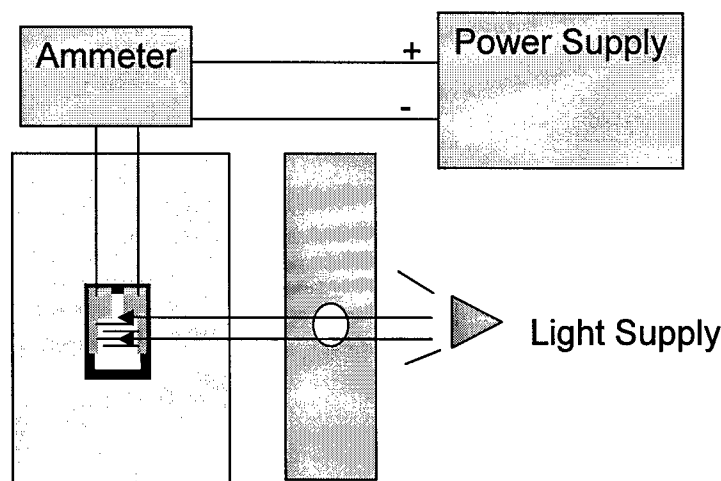
**a)**



**b)**

**Figure 7: Optical microscope image of the PECH/carbon black fibers on a gold substrate (a) and a microelectrode (b)**

### Infrared Sensors:

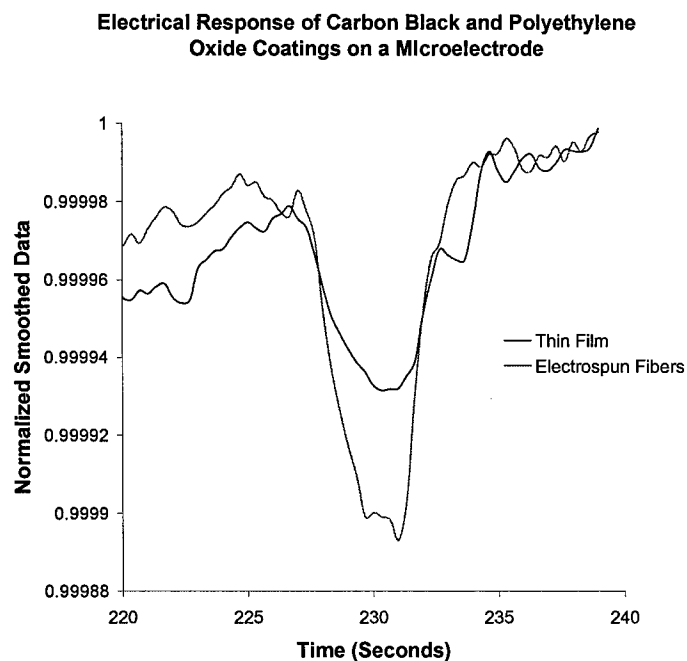


**Figure 8: Schematic diagram of infrared sensor testing apparatus**

An infrared sensor was developed consisting of an array of PEO fibers doped with carbon black and deposited onto the surface of the microelectrode. A control sensor consisting of the same polymer composite in the form of a uniform film was also developed and tested. The resulting sensors were tested using the microelectrode infrared testing station (METS) illustrated in figure 7. The METS measures the change in sensor current at constant voltage under infrared illumination.

Figure 9 is a plot of the normalized IR response curves for both the thin film and electrospun fibers. As can be seen in the figure, the sensitivity of the fiber array was significantly greater than the sensitivity of the thin film. The enhanced sensitivity is due, in part, to the much higher surface to volume ratio of the fiber arrays in comparison to the uniform film. These initial fibers are larger than one micron in diameter and at this time we do not have any data on the effect of fiber diameter on the sensor performance. One of the primary objectives of the next year of the project is to investigate the relationship between sensor architecture and composition on performance variables such as sensitivity and response time.





**Figure 9: IR response curves for thin film and fiber array**

**Chemical Sensors:**

A new electronic nose based on a four-component array of chemically responsive, electrically conducting polymer fiber composites was developed and tested. Figure 10 is a photograph of a typical sensor element next to a dime for size comparison.



**Figure 10: Photograph of chemical sensor microelectrode.**

Microscale fibers from four different polymer composites were electrospun directly onto the surface of microelectrodes consisting of interdigitated gold strips deposited onto a glass substrate. The fibers consisted of a polymer/carbon black blend near the percolation threshold.

The resulting sensor array was tested upon exposure to four different analyte vapors including one alcohol, two organic solvents and one chemical warfare agent simulant. The sensitivity and response kinetics for each sensor element was measured for each vapor. The response pattern from the four-component array was measured and was distinct for each vapor.

Poly(epichlorohydrin) (PECH),  $M_w$  of 700,000, poly(ethylene Oxide) (PEO)  $M_w$  of 400,000 Daltons, poly(isobutylene) (PIB)  $M_w$  of 500,000 Daltons and poly(vinylpyrrolidone) with a  $M_w$  of 1.3 million were purchased from Aldrich and the carbon black (Black Pearls 2000) was purchased from Cabot labs. For the PEO and PVP the electrospinning solution was an 8.0 % w/w of polymer in DI water. A 9% by wt. of PIB was dissolved in toluene and the PECH was dissolved in chloroform at 9 wt%. For all polymer formulations carbon black was added to provide a dry solids ratio of 80/15 of polymer/CB by wt.

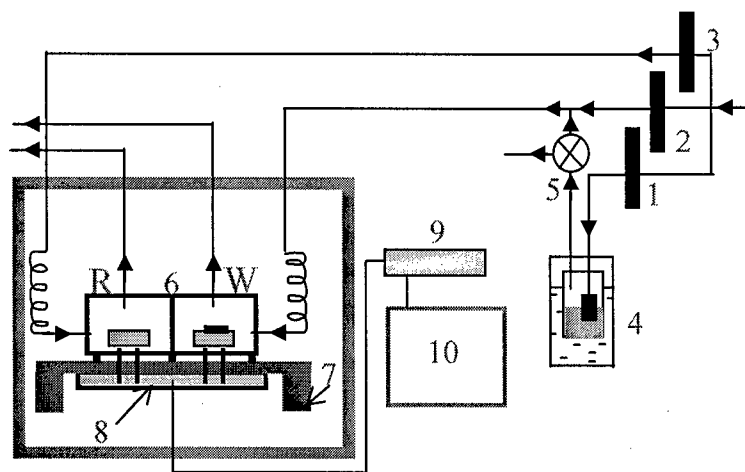
The electrospinning configuration is a 30 gauge blunt needle fit into a 1 ml plastic or glass syringe charged to  $\sim 5$ -7kV DC (+) at the tip, with the target 2 to 3 cm away. For electrospinning the PEO and PVP solutions a plastic syringe was used while a glass syringe was used for the PIB and PECH solutions. Also, the PECH solution is solid at room temperature so it is necessary to liquefy the solution by heating to approximately 50 degrees Celsius before use.

The microelectrode substrates consist of an interdigitated array of 15  $\mu\text{m}$  wide gold electrodes deposited onto glass and were attached to a grounded counter electrode consisting of a hexagonal rotating drum (1725 rpm). The electrospun fibers are wound around the rotating drum and collected on the microelectrode. The flow rate of the polymer composite solution was approximately 4 microliters/min and was controlled by a Harvard Apparatus PUD 2000 Infusion syringe pump.

The chemical testing was performed using a custom-built Chemical Microelectrode Testing Station (CMTS) shown in figure 11. The CMTS specifically measures the change in current at constant voltage of the microelectrode during exposure to a test vapor at a controlled concentration. The primary components of the CMTS consist of a Pentium II computer, Agilent 34970A Datalogger, Agilent Programmable Power Supply E3631A, VWR Heating/Cooling Bath, Aalborg Gas Flow Controllers, Nitrogen Carrier Gas, LabView software and GPIB interface.

The sensor elements were placed in a chamber for vapor exposure. A potential was placed across the sensor element and the current was measured. Nitrogen was used both as a carrier gas and diluant. The carrier stream was passed through a U-Tube bubbler containing the analyte. A cooling bath was used to control the vapor pressure of the

analyte and was typically 10.0 Celsius in the experiments described here. The nitrogen/analyte gas stream was mixed with a pure nitrogen stream in order to control the analyte concentration. The current through the sensor element was monitored as a function of time during exposure to the analyte. During the testing the sensor element was at ambient temperature.

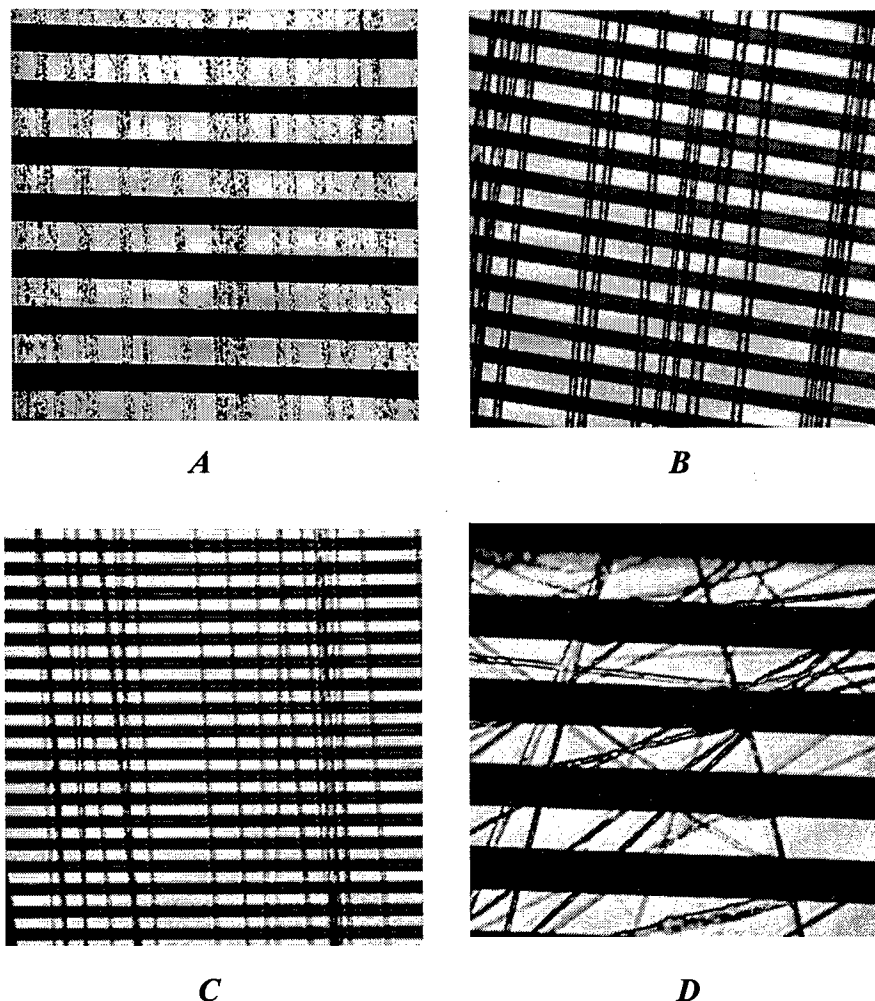


**Figure 11: Chemical Sensor Calibration System**

### Chemical Sensor Results

Figure 12 is a series of light microscope images of the PEO, PIB, PECH and PVP fiber arrays on the surface of the interdigitated microelectrodes. The fibers range in diameter from about 1 to 5 microns for the images of figure 12 and we have found that the fiber diameter for each polymer composite depends primarily on the concentration of the polymer in the electrospinning solution. This finding is consistent with the literature on electrospinning. A detailed investigation on the relationship between fiber diameter and sensor performance is beyond the scope of this manuscript and will be the subject of a follow on paper. It is important to note, however, that the sensor response time, just as in film based sensors, is expected to improve with decreasing fiber diameter and the electrospinning process is capable of producing fibers with extremely small diameters in the range of 50nm. By carefully controlling the electrospinning conditions, aligned arrays of PECH, PEO and PIB fiber composites were produced and aligned in a direction running perpendicular to the gold electrodes. A high degree of fiber alignment in electrospinning is somewhat unusual, because the charged fibers are inherently unstable and normally oscillate violently producing a non-woven mat of fibers with random orientations. Recently, however, it has been demonstrated that, by controlling specific

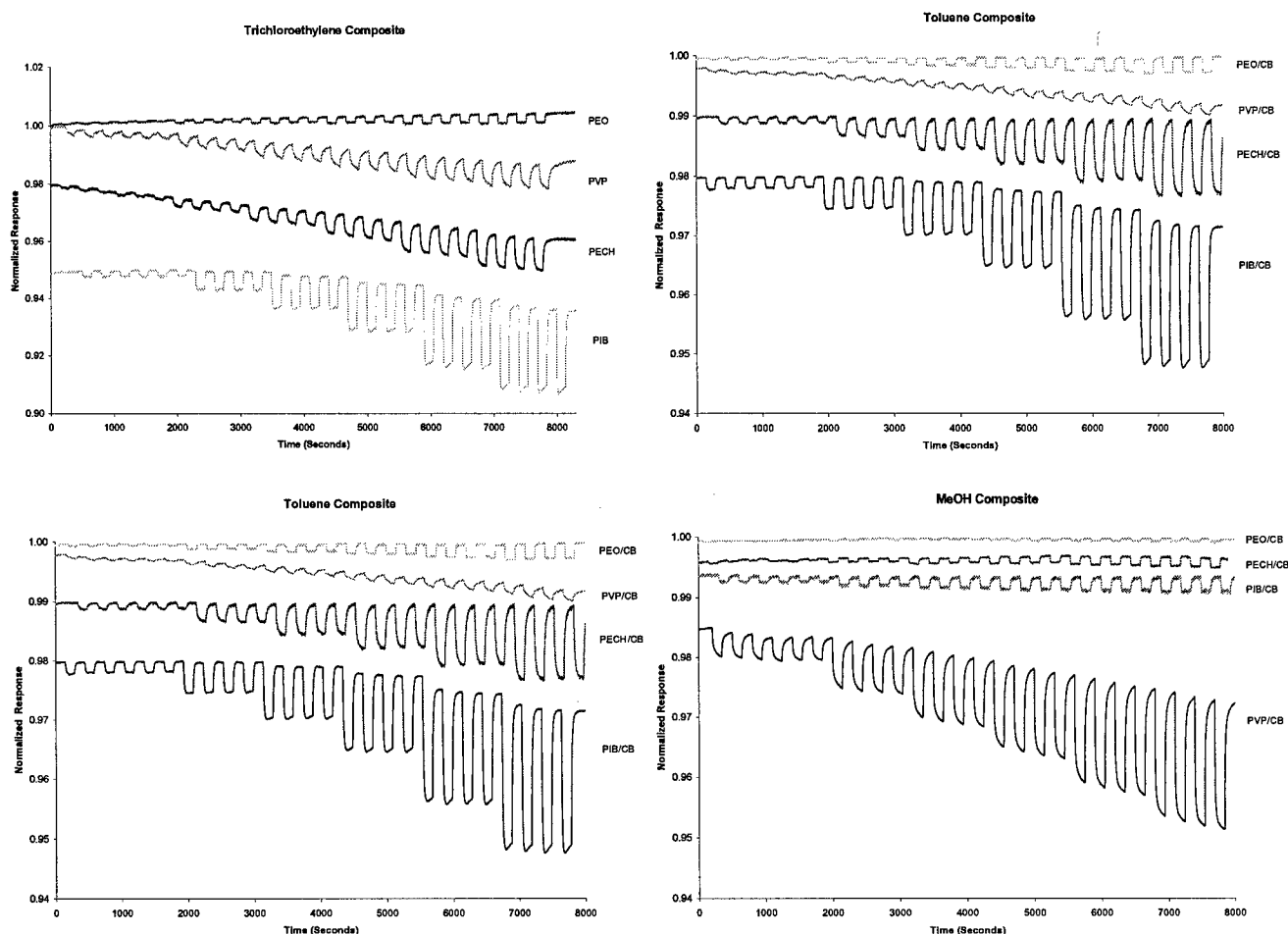
processing conditions, it is possible to produce aligned arrays of fibers using electrospinning. The PVP fibers illustrated in figure 3D are randomly oriented as is more typical of electrospun fibers and we are continuing to work with this system in order to improve the fiber alignment in the PVP sensor element.



**Figure 12:** Optical microscope images of the sensor element consisting of a) PEO b) PIB c) PECH and d) PVP composite fibers on the surface of the interdigitated microelectrodes (electrode spacing:  $15\mu\text{m}$ ).

In all four sensor elements the coverage of the electrospun fibers as depicted in figure 12 is uniform across the entire microelectrode surface. The net electrical resistance of the sensor element depends upon the individual fiber resistance and fiber density and ranged from 10 to 100 Ohms for all of the sensor elements reported in this manuscript. Because the fibers are deposited across an interdigitated electrode, the net electrical resistance of a sensor element is actually the sum of  $N$  individual parallel fibers. Optical microscopy was used to estimate the number of fibers on each sensor electrode in order to determine

the electrical resistance of a single fiber. For all four composite fibers studied, the electrical resistance of an individual fiber fell between  $10^5$  and  $10^6$  Ohms. Assuming that the fiber length is equal to the interdigitated electrode spacing (15 microns) and using a typical fiber diameter of 3 microns, we estimate that the electrical resistivity of the electrospun composite fibers falls in the range of  $10^{-1}$  to  $10^{-2}$  Ohm-m, which is similar to that of a semiconducting material such as elemental Germanium.

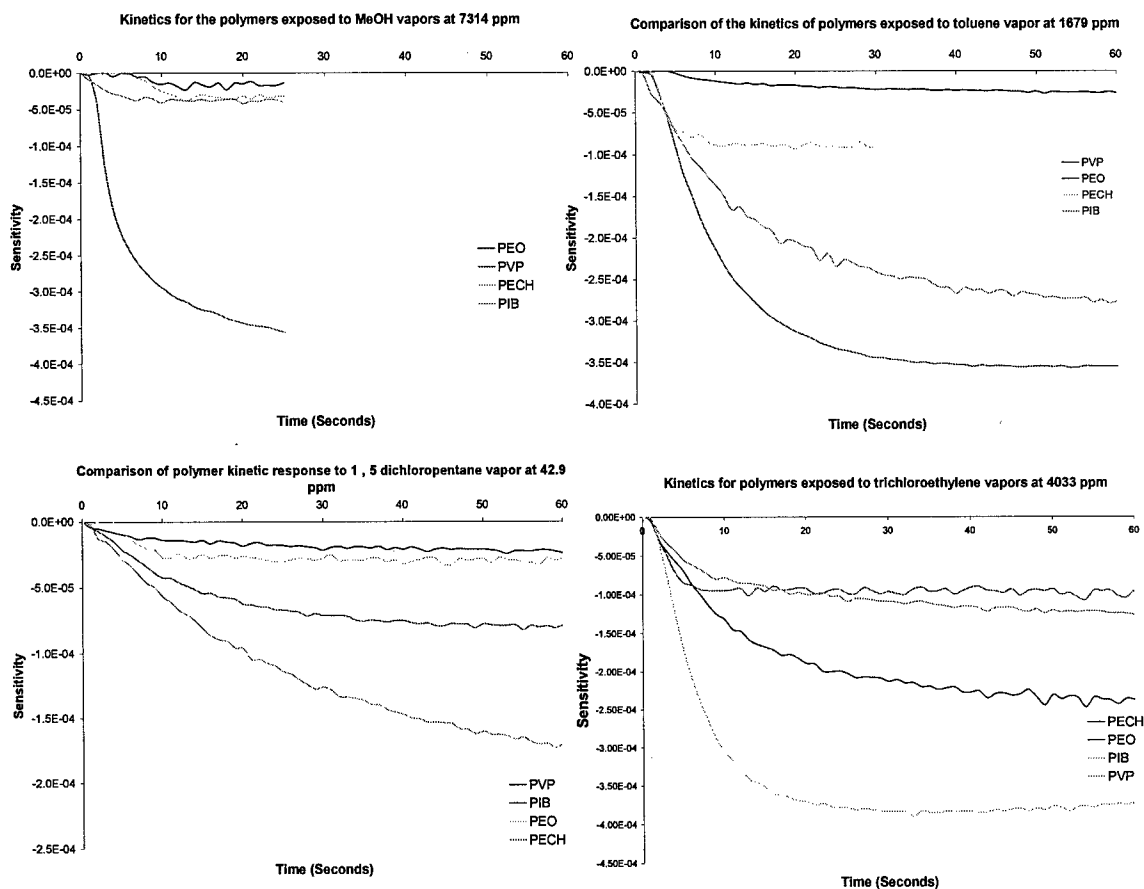


**Figure 13: Raw sensor output data as a function of time for each sensor element exposed to four different analyte vapors at several different and increasing concentration.**

Figure 13 is a plot of the normalized raw sensor output versus time for each of the four sensor elements exposed to periodic cycles of the four analyte vapors at increasing concentrations. In each case the analyte was cycled on and off several times at each concentration. The baseline drift seen in some of the data of figure 13 is an indication that vapor desorption is incomplete between each cycle.

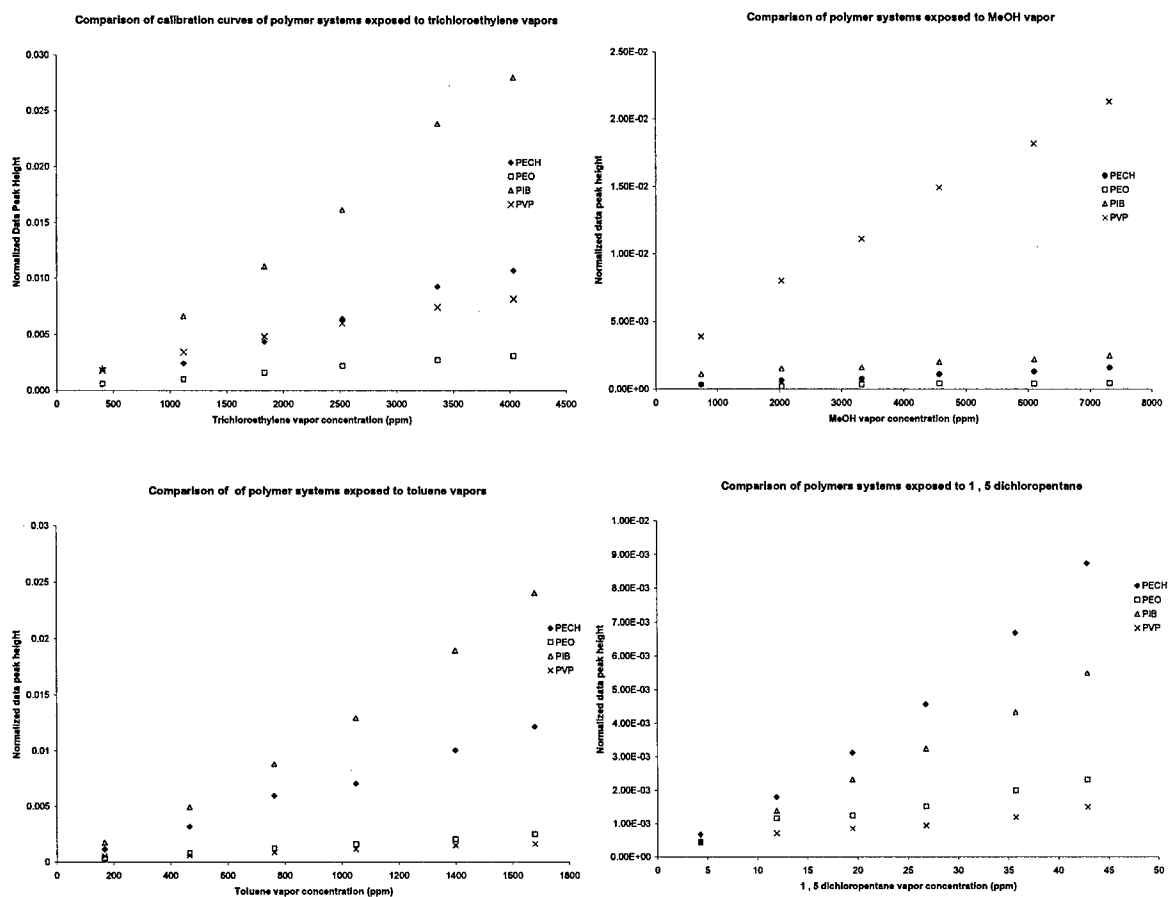
The response time of each sensor element was measured in response to each test vapor at one particular concentration and is illustrated in figure 14. In general the response time

will depend on both the fiber diameter as well as the vapor permeation rate of through the polymer composite. For the data presented in figure 14, with the exception of the dichloropentane response, the response time (time to reach 90% of the steady state value) was less than 60 seconds.



**Figure 14: Sensor output response versus time for each sensor element exposed to four different analyte vapors.**

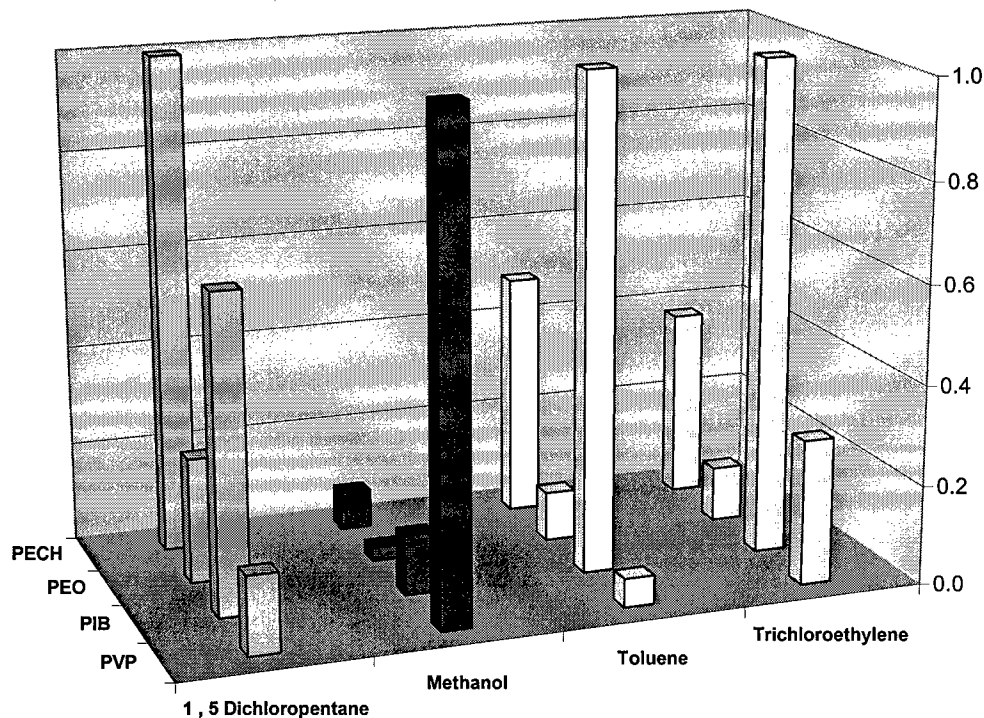
The sensor response magnitude as a function of vapor concentration was measured for each test vapor and is illustrated in figure 15. The output response for each sensor element was linear with concentration indicating the absence of saturation effects. The sensitivity of a given sensor element to a particular vapor is determined from the slope of the response curve of figure 15 and varies significantly depending on the chemical affinity of a particular polymer to a particular analyte vapor.



**Figure 15: Sensor response magnitude versus vapor concentration for four different analyte vapors.**

Figure 16 is a three dimensional graph of the sensor array response pattern to each of the four analyte vapors. The response pattern provided a unique fingerprint for each of the four vapors.

3D graph of polymer responses to vapors

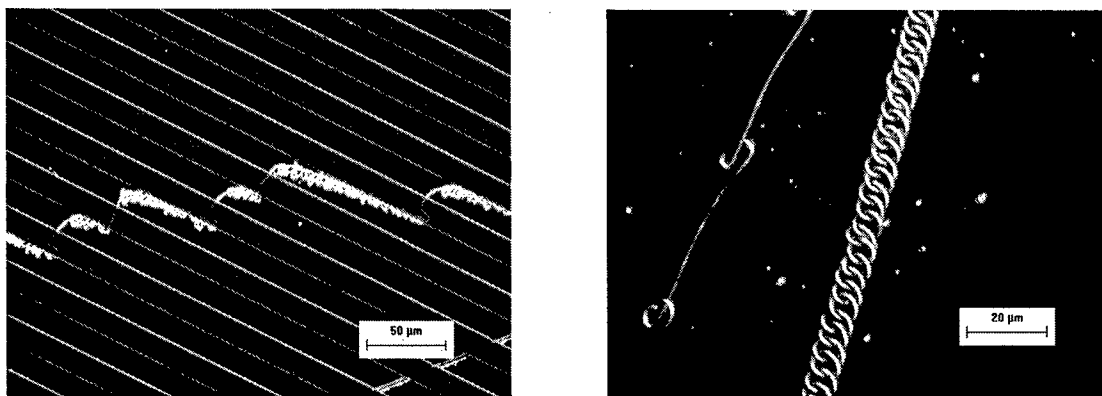


**Figure 16: 3D graph of sensor array response pattern to four different analyte vapors**

### Helical Structures:

Microscale helical coils consisting of a composite of one conducting and one non-conducting polymer were produced using electrospinning. The non-conducting polymer was Poly(Ethylene Oxide) and the conducting polymer was Poly(Aniline Sulfonic Acid). The coil structures were studied over a range of processing conditions and fiber composition. The data suggest that the helical structures are formed due to viscoelastic contraction upon partial neutralization of the charged fibers. These polymeric microcoils may find applications in microelectromechanical systems (MEMS), advanced optical components and drug delivery systems. Figure 17 shows two optical microscope images of some typical helical structures. Figure 17a shows a pattern of helical structures deposited onto the surface of an interdigitated microelectrode and figure 16b shows helical structures deposited onto the surface of a gold substrate. This work was published and is described in detail in Applied Physics Letters.

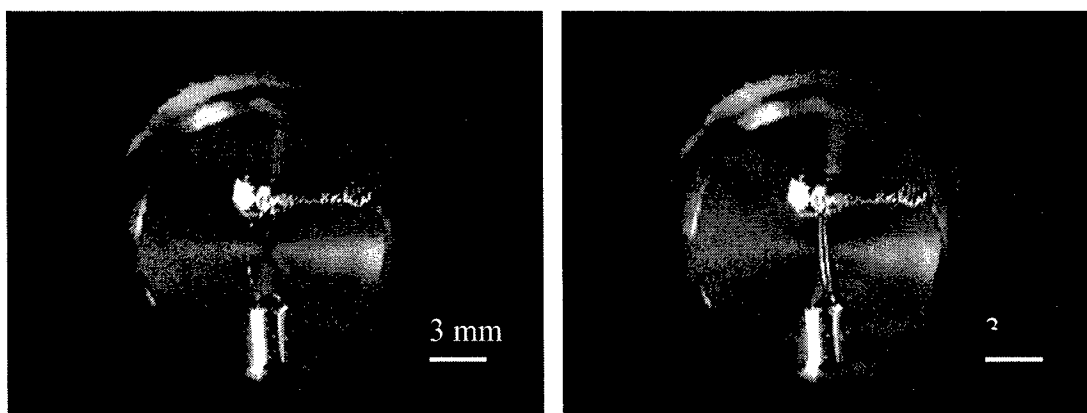




**Figure 17:** Optical microscope images of helical structures on an interdigitated electrode (a) and a gold substrate (b)

#### **Supercritical Fluid Assisted Electrospinning:**

Polymer fibers of high molecular weight polydimethylsiloxane (PDMS) and Poly (D,L-lactic acid) (PLA) were produced using only electrostatic forces and without the use of a liquid solvent. The fibers were formed between two electrodes in a high-pressure view cell. A polymer sample was placed on a grounded electrode and a second, counter electrode was placed at high potential. The polymer was observed as the thermodynamic conditions (e.g. temperature, CO<sub>2</sub> pressure) and potential difference were varied. At a CO<sub>2</sub> temperature and pressure above the critical point, but well below the single-phase region, polymer fibers formed between the grounded electrode and the high voltage counter electrode. It is surmised that the supercritical CO<sub>2</sub> reduces the polymer viscosity sufficiently to allow fibers to be electrostatically pulled from an un-dissolved bulk polymer sample. Figure 18 is a photograph illustrating two PLA fibers of different diameter produced using this technique. This work was published and is describe in detail in the Journal of Supercritical Fluids.



**Figure 18:** PLA fibers produced using supercritical fluid assisted electrospinning

## **Personnel Supported:**

### **At Sentor Technologies Inc.**

Dr. Royal Kessick, Principal Investigator  
Dr. Dmitry Pestov, Senior Scientist  
Mr. Hugh Maupin, Technician  
Mr. Byron Smith, Technician  
Dr. Gary Tepper, Senior Scientist

### **At Virginia Commonwealth University**

Dr. John Fenn, Principal Investigator and Professor of Chemistry  
Mr. Pavel Kiselev, Graduate Student

## **Publications:**

### **Peer Reviewed Journal Publications:**

Royal Kessick and Gary Tepper, "Electrospun Polymer Composite Fibers for the Detection of Volatile Organic Compounds", *Sensors and Actuators* - submitted

Royal Kessick and Gary Tepper, "Microscale Polymeric Helical Structures Produced by Electrospinning", *Applied Physics Letters*, 84(24), (2004)

Natalia Levit and Gary Tepper, "Supercritical CO<sub>2</sub> -Assisted Electrospinning", *The Journal of Supercritical Fluids*, 31(3) 329-333 (2004)

R. Kessick and G. Tepper, "Microscale Electrospinning of Polymer Nanofiber Interconnections", *Applied Physics Letters*, 83, no.3, (2003).

### **Interactions/Transitions:**

G. Tepper, "Chemical Microsensors based on Polymer Nanofiber Composites", SPIE Defense and Security Symposium, Orlando, FL (April 2005)

R. Kessick, J. Fenn and G. Tepper, "Biomimetic Chemical Sensors Based on Electrospun Fiber Arrays", Proceedings of the AFOSR Meeting on Molecular Dynamics and Theoretical Chemistry (2005)

G. Tepper, R. Kessick and J. Fenn, "Polymer Nanowire Arrays for Sensing Applications", AFOSR Molecular Dynamics and Theoretical Chemistry Conference, May 2004, Providence, RI

G. Tepper, R. Kessick and J. Fenn, "Polymer Nanowire Arrays for Sensing Applications", AFOSR Molecular Dynamics and Theoretical Chemistry Conference, May 2003, San Diego, CA